

[Name of the Document] Specification

[Title of the Invention] Phenolic Resin Composite Material

[Scope of the Patent Claim]

[Claim 1] A phenolic resin composite material, comprising: a phenolic resin; and a filler dispersed in the phenolic resin and being a reinforcement member,

wherein it is characterized in that an organized layered clay mineral being different from said filler is dispersed uniformly in said phenolic resin.

[Claim 2] The phenolic resin composite material according to claim 1, wherein said phenolic resin is a resol type phenolic resin.

[Claim 3] The phenolic resin composite material according to claim 1, wherein said filler is either one of glass fibers, calcium carbonate and wooden powders.

[Claim 4] The phenolic resin composite material according to claim 1, wherein said organized layered clay mineral is a sodio-montmorillonite which is organized by an organic onium ion.

[Claim 5] The phenolic resin composite material according to claim 1, wherein said filler and said organized layered clay mineral are contained in a summed amount of 75% by mass or less when the entirety is taken as 100% by mass.

[Detailed Description of the Invention]

{0001}

[Technical Field to which the Invention Belongs]

The present invention relates to a phenolic resin composite material, which is good in terms of heat resistance, etc., and which is applicable to automotive component parts, aircraft component parts,

component parts for electric-electronic instruments, materials for architecture, and so on.

【0002】

【Prior Art】

Phenolic resins have been used widely in resinous molded products, but most of them have been used as composite materials. And, in order to improve the mechanical strengths of the resinous molded products, organic fillers, such as cotton, wooden powders, etc., inorganic fibers, such as glass fibers, carbon fibers, etc., and further inorganic fillers, such as clays, calcium carbonate, etc., have been mixed in phenolic resins.

However, even when inorganic materials, and the like, are simply added-mixed in phenolic resins; they bond very weakly with the phenolic resins which make a mother phase, when fillers are added, it might be probable to cause such a problem as the embrittlement of composite materials.

Therefore, for the purpose of strengthening the bonding between phenolic resins and inorganic materials, it has been known to treat inorganic materials with silane coupling agents, for example, even in such a case, the bonding between them results from the van der Waals force, and it is such an extent only that the affinity between them is improved. Thus, in conventional phenolic resin composite materials, it has not been possible to sufficiently improve the reinforcement effect and heat resistance.

【0003】

Moreover, there is a disclosure on a composite material in which a layered clay mineral is dispersed in a phenolic resin in Japanese

Patent Publication No. 3,014,674. Specifically, in the examples, a composite material is disclosed in which a layered clay mineral (montmorillonite), being turned into an onium salt, is mixed in a phenolic resin. In the case of this composite material, since the phenolic resin and the layered clay mineral undergo ion bonding, hydrogen bonding or both of them, it is said to exhibit better mechanical strengths and heat resistance.

[0004]

[Assignment to be Solved by the Invention]

However, even such a phenolic resin composite material has been still insufficient in terms of the mechanical strengths, especially, the high temperature strength, and consequently phenolic resin composite materials, which can exhibit much better heat resistance, have been required.

The present invention has been done in view the circumstances, and it is an object to provide a novel phenolic resin composite material which is much better in terms of the mechanical strengths, especially the heat resistance, than conventional ones and whose usable ranges are wide.

[0005]

[Means for Solving the Assignment]

Hence, the present inventors studied earnestly to solve the assignment, and repeated trial and error over and over again, as a result, they found out that it was possible to further improve the heat resistance of phenolic resin composite material by dispersing an organized layered clay mineral uniformly in a phenolic resin with a filler dispersed, organized layered clay mineral which was different

from the filler, and arrived at completing a phenolic resin composite material according to the present invention.

Namely, the present phenolic resin composite material comprises: a phenolic resin; and a filler dispersed in the phenolic resin and being a reinforcement member,

wherein it is characterized in that an organized layered clay mineral being different from said filler is dispersed uniformly in said phenolic resin.

[0006]

Layered clay minerals usually have a layered structure in which a large number of sheets are laminated, however, in the case of the organized layered clay mineral set forth in the present invention, the respective layers are disassembled, are turned into a sheet shape (or a sheet shape in which an extremely small number of them are laminated) for every layer, are dispersed uniformly in the phenolic resin, and are bonded strongly to the phenolic resin by ion bonding, by hydrogen bonding or by both of them, and consequently it is believed that a cross-linked structure is formed between it and the phenolic resin.

In other words, it is believed that the organized layered clay mineral is such that the bonding forces (the van der Waals force, the electrostatic attraction force, and the like) for the respective layers are overcome; it is completely separated for each of the layers to exist independently; and both of them are strongly bonded by ion bonding between negative charges possessed by their layers and positive charges possessed by the end groups or side chains of the phenolic resin, by hydrogen bonding between polar groups of the clay

layers and polar groups of the phenolic resin, or by both of them.

And, in the case of the present phenolic resin composite material, since the dispersion of the organized layered clay mineral is done in the phenolic resin in which the filler being the reinforcement member is dispersed, it is believed that the organized layered clay mineral and the filler produce a synergistic effect so that a phenolic resin composite material can be obtained which is unconventionally good in terms of the mechanical strengths, especially in terms of the heat resistance.

【0007】

【Mode for Carrying out the Invention】

Next, while referring to preferred embodiments, the present invention will be described in more detail.

(1) Organized Layered Clay Mineral

① The organized layered clay mineral refers to a layered clay mineral which is organized by an organic onium ion.

For example, as the organized layered clay mineral, there is a sodio-montmorillonite, and the like, which is organized by an organic onium ion. Since the sodio-montmorillonite exists widely in the natural environment and its cost is stable, it is preferable as a raw material for the organized layered clay mineral.

【0008】

② Layered Clay Mineral

The layered clay mineral refers to a so-called layered phyllosilicate.

For instance, there are smectite-based clay minerals, such as montmorillonite, saponite, hectorite, beidellite, stevensite,

nontronite, etc., vermiculite, halloysite, swelling micas, kaolinite, and so on.

These can be either natural ones or synthesized ones.

【0009】

③ The organic onium ion is such that the number of carbon atoms is 6 or more, for example, an alkyl onium ion is representative. When the number of carbon atoms is less than 6, the hydrophilic property of the organic onium ion is heightened so that there might arise a fear in that the compatibility of the organized layered clay mineral decreases with respect to the phenolic resin.

The onium ion can be primary through quaternary ammonium ions, for instance, it is possible to use hexyl ammonium ion, octyl ammonium ion, 2-ethylhexyl ammonium ion, dodecyl ammonium ion, lauryl ammonium ion, octadecyl ammonium ion, dioctyl dimethyl ammonium ion, trioctyl ammonium ion, dioctadecyl dimethyl ammonium ion, trioctyl ammonium ion, dioctadecyl dimethyl ammonium ion, trioctadecyl ammonium ion, and the like.

Moreover, it is possible to use phosphonium ions. As the phosphonium ion, for example, it is possible to use tetraethyl phosphonium ion, triethyl benzyl phosphonium ion, tetra-n-butyl phosphonium ion, tri-n-butyl hexadecyl phosphonium ion, tri-n-butyl benzyl phosphonium ion, and so on.

【0010】

④ The layered clay mineral is such that, in order that the respective layers are separated to uniformly disperse in the phenolic resin, the inter-layers can preferably be swelled greatly, and it is preferable to make a cation exchange capacity of the layered clay

mineral from 50 to 200 milli-equivalent/100 g, further from 70 to 150 milli-equivalent/100 g.

When the cation exchange capacity is less than 50 milli-equivalent/100 g, since the organization of the layered clay mineral by means of ion exchange with the organic onium ion is likely to be insufficient, there might arise a possibility in that the swelling of the layered clay mineral is difficult eventually.

On the other hand, when the cation exchange capacity exceeds 200 milli-equivalent/100 g, since the number of bonds between the negative charges of the clay layers and the cations disposed between the clay layers increases, the bonding forces between the layers of the layered clay mineral are strengthened so that the intervention between the layers by means of ion exchange with the organic onium ion is difficult, and there might arise a possibility in that the swelling of the layered clay mineral is insufficient eventually.

[0011]

(2) Phenolic Resin

As for the phenolic resin, resol type and novolak type can be exemplified, however, either one of them can be used, or both of them can be mixed to use.

In a case where the phenolic resin composite material is cured to use, when a resol type phenolic resin is used, it is suitable because a curing agent, etc., are not needed separately, and because the adverse influence, which results from a curing agent, to the dispersion property of the layered clay mineral can be avoided.

In a case where the phenolic resin composite material is used without curing, when a novolak type phenolic resin is used, it is

suitable because the self-condensation reaction hardly arises, and because useless side reactions can be avoided. In particular, it is suitable when it is mixed with another resins, which will be described later.

【0012】

(3) Filler

The filler is such that, as far as it is a reinforcement member which is filled in phenolic resins, the species can be either organic materials or inorganic materials. Therefore, for instance, the filler is such that, as far as it is glass fibers, calcium carbonate, wooden powders, cotton, or organic fibers, such as polyester fibers, polyamide fibers, polyvinyl alcohol fibers, aromatic polyamide fibers, carbon fibers, etc., or organic or inorganic fillers, which are usually used, they can be either independent or mixtures. However, when glass fibers, calcium carbonate or wooden powders are used as the filler, since they are less expensive than organic fibers, and so on, and since they can be included in a large amount and can thereby enhance the heat resistance, it is further preferable. Among them, the usage of glass fibers is most preferable. This is because glass fibers are such that a higher reinforcement effect can be obtained with a smaller amount compared with calcium carbonate and wooden powders.

Incidentally, the above-described filler and organized layered clay mineral are such that it is preferable to be contained in a summed amount of 75% by mass or less when the entire phenolic resin composite material is taken as 100% by mass.

When they exceed 75% by mass, the phenolic resin becomes less

than 25% by mass so that it is difficult to manufacture a phenolic resin composite material which can stably sustain the heat resistance. When a summed amount of the filler is from 30 to 65% by mass, it is further preferable. Moreover, it is preferable as well to make the organized layered clay mineral from 2 to 65% by mass, further from 2 to 10% by mass.

【0013】

(4) Uses

The phenolic resin composite material according to the present invention can be used for a variety of products in a diversity of fields, such as automotive component parts, aircraft component parts, component parts for electric-electronic instruments, materials for architecture, and so on. In particular, by making use of the good heat resistance, it is preferable to use it for component members which are used in high-temperature environments, for example, taking automotive component parts, covers or stays in engine rooms, pulleys such as tensioner pulleys, power steering pulleys or pulleys for compressors. When the phenolic resin composite material is applied to such uses, depending on the uses, reforming materials can be added. As the reforming materials, elastomers and rubbers can be exemplified. These reforming materials are such that the phenolic resin comprising the filler and the organized layered clay mineral can be added in an amount of from 0.05 to 70 parts by weight with respect to 100 parts by weight.

Moreover, when being applied to the aforementioned uses, the phenolic resin composite material is mixed with thermoplastic resins, and can be used as a reforming material for thermoplastic resins.

As the thermoplastic resins, polyamide resins, polyolefin resins, polyester resins, polyphenylene ether resins, and so on, can be exemplified. When being used as a reforming material for these thermoplastic resins, from 0.05 to 50 parts by weight can be added with respect to 100 parts by weight of the thermoplastic resins. As a reforming material for thermoplastic resins, the above-described novolak type phenolic resin is suitable.

【0014】

(Examples)

Next, while naming examples, the present invention will be described in much more detail.

(Examples)

(1) Manufacture of Samples and Test Pieces

① Manufacture of Organized Clay (Organized Layered Clay Mineral)

As the layered clay mineral, a sodio-montmorillonite (produced by KUNIMINE KOGYO Co., Ltd), moreover, as the organic onium salt, octadecyl ammonium were used, respectively. They were stirred-mixed in water, and the clay was ion-exchanged with the octadecyl ammonium ion (the organic onium ion) so that the cation exchange capacity became 110 milli-equivalent/100 g, thereby manufacturing an organized clay.

【0015】

② Adjustment of Formed Materials

As the phenolic resin, a resol type phenolic resin (SUMITOMO BAKELITE Co., Ltd) with an additive agent added was used, and was compounded with a variety of fillers, set forth in Table 1, as well as the above-described organized clay in proportions, set forth in

Table 1, and was kneaded by means of thermal roll, thereby obtaining formed materials of Sample Nos. 1 through 8 set forth in Table 1. Note that the proportions in Table 1 are % by mass.

【0016】

③ Forming of Test Pieces

By using the formed materials of above-described Sample Nos. 1 through 8, bending test pieces (4 × 10 × 80 mm), defined in JIS (K6911), were formed with a compression molding machine whose mold clamping force was 35 ton (343 kN), respectively, under the conditions of mold temperature: 175 °C × curing time: 3 minutes × forming pressure: 15 MPa.

【0017】

【Table 1】

Sample No.	1	2	3	4	5	6	7	8
Filler		Glass Fiber		Calcium Carbonate		Wooden Powder		
	50%	45%	40%	50%	45%	40%	50%	45%
	0%	5%	0%	0%	5%	10%	0%	5%
Organized Clay	0%	←	←	←	←	←	←	←
Matrix Resin	45%							
Phenolic Resin (Resol Type)								
Additive	5%	5%	5%	5%	5%	5%	5%	5%

[0018]

(2) Observation of Dispersing State of Organized Clay

In order to observe the dispersing state of the organized clay, a tiny specimen was cut out of the formed material of Sample No. 8, and an x-ray diffraction measurement was carried out under the conditions set forth in Table 2. A diffraction chart in this instance is illustrated in Fig. 1. Moreover, the result of an x-ray diffraction measurement, which was performed onto a clay simple substance before the organizing under the same conditions, is illustrated in Fig. 2 for reference. Note that the horizontal axis of Fig. 1 and Fig. 2 is diffraction angles ($^{\circ}$) and the vertical axis is intensities of x-ray.

As can be understood from Fig. 2, in the case of the clay simple substance, a peak, which resulted from the layered structure was clearly observed in the diffraction chart. However, as can be understood from Fig. 1, in the case of the formed material of Sample No. 8 of the present example, no peak was appreciated in the diffraction chart. Thus, it is believed that, in the phenolic resin composite material of the present example, the layer interfaces of the clay are opened, and the clay has not already taken a layered structure and is dispersed uniformly in the phenolic resin.

【0019】

【Table 2】

X-ray Source	Cu-K α
Tube Voltage-Tube Current	30 kV, 30 mA
Slit	DS 0.17, RS 0.15, SS 0.17
Apparatus	"RAD-B" Made by RIGAKU DENKI Co., Ltd.

【0020】

(3) Evaluation of Heat Resistance

① Weight Reduction Temperature

A weight reduction temperature, which becomes one of the indexes of heat resistance, was measured. Namely, tiny specimens were cut out of the formed materials of the respective samples, and were measured for weight reductions by using a thermobalance "TG/DTA220" (produced by SEIKO ELECTRIC Co., Ltd.). This measurement was carried out in an air flow at a temperature increment rate of 10 °C/min.

In Table 3, there are set forth 5% and 10% weight reduction temperatures, which were obtained regarding the specimens of the respective samples.

When the filler was the glass fiber (Sample Nos. 1 through 3) and when the filler was the calcium carbonate (Sample Nos. 4 through 6), it is understood that, by adding the clay, the 5% weight reduction temperatures and 10% weight reduction temperatures increased apparently and the heat resistance was improved.

【0021】

In any case, when the filler was the wooden powder (Sample Nos. 7 and 8), the increment of the weight reduction temperature was not observed. However, this is believed to result from the decomposition of the wooden powder, which is an organic component, at a low temperature, and it is understood from a later-described bending strength retention ratio that this does not deny the heat resistance improvement of the phenolic resin composite material whose filler is a wooden powder.

【0022】

② Long Term Degradation

The high temperature durability and high moisture durability regarding the mechanical strength of the phenolic resin composite material were examined, high temperature durability and high moisture durability which become the other indexes of the heat resistance. Namely, regarding the respective JIS bending test pieces, which were formed of Sample Nos. 2 through 8, the bending strengths before and after being left at 150 °C (in air) × 1,000 hours as well as the bending strengths before and after being left at 50 °C (in air) × 95% (moisture) × 1,000 hours were measured, and the retention ratios of the bending strengths were determined from the measurement values before and after being left. The results are illustrated in Fig. 3. Note that the measurement was carried out by using an autograph (produced by SHIMAZU SEISAKUSHO Co., Ltd.).

【0023】

From the results, regardless of organic or inorganic, the phenolic resin composite materials, which used whatever fillers, were such that the strength retention ratios were improved. In particular,

the bending strength retention ratios of the test pieces were greatly improved, test pieces which comprised the samples with the clay added in an amount of 10%.

Regarding the reason why the heat resistance of the phenolic resin composite materials of the present examples is improved, it has not necessarily been clarified yet at present, however, as a revelation mechanism, it is believed that the respective layers of the clay are dispersed uniformly in the phenolic resin and thereby the effect of inhibiting the oxidation degradation of the phenolic resin is revealed.

(0024)

[Table 3]

Sample No.	1	2	3	4	5	6	7	8
5% Weight Reduction Temp. (°C)	333.5	346.2	342.9	341.5	348.8	352.2	239.6	238.3
10% Weight Reduction Temp. (°C)	372.1	419.2	424.4	381.2	425.4	422.0	297.1	296.0

【0025】

【Effect of the Invention】

In accordance with the present invention, a further improvement of the heat resistance of phenolic resin composite materials can be intended, and the application expansion of phenolic resin composite materials can be intended.

【Brief Description of the Drawings】

【Fig. 1】 is an x-ray diffraction chart of an example according to the present invention.

【Fig. 2】 is an x-ray diffraction chart of the clay simple substance which was used in manufacturing the example.

【Fig. 3】 is a diagram for illustrating the bending strength retention ratios in the long term degradation test which was carried out on a variety of phenolic resin composite materials.

【Name of Document】 Abstract

【Abstract】

【Assignment】 To provide a new phenolic resin composite material which can intend an improvement of the heat resistance or mechanical strength.

【Means for Solution】 A phenolic resin composite material comprises: a phenolic resin; and a filler dispersed in the phenolic resin and being a reinforcement member,

wherein it is characterized in that an organized layered clay mineral being different from said filler is dispersed uniformly in said phenolic resin.

【Selected Drawing】 Fig. 3